

Natural Orbital Functional Theory and Pairing Correlation Effects in Electron Momentum Density

B. Barbiellini

Department of Physics, Northeastern University, Boston, MA 02115 USA

Abstract

Occupation numbers of natural orbitals capture the physics of strong electron correlations in momentum space. A Natural Orbital Density Functional Theory based on the antisymmetrized geminal product provides these occupation numbers and the corresponding electron momentum density. A practical implementation of this theory approximates the natural orbitals by the Kohn-Sham orbitals and uses a mean-field approach to estimate pairing amplitudes leading to corrections for the independent particle model. The method is applied to weakly doped La_2CuO_4 .

A key characteristic of an interacting electron system is the electron momentum density (EMD). For metallic systems one can also define the Fermi Surface (FS) as the break in the EMD whose presence reveals the existence of quasi-particles and the validity of the Landau-Fermi liquid theory [1]. FS studies are particular needed in the field of high temperature superconductivity. Figure 1 shows the calculated FS of the well known $\text{HgBa}_2\text{CuO}_4$ [2] while Figure 2 illustrates the evolution of the FS topology with doping of a less known compound studied by Jarlborg *et al.* [3]. One can notice in Fig. 2 a topological transition (also called Lifshitz transition), which does not involve any symmetry breaking [4].

Positron annihilation has been successful for the determination of the FS in many metallic systems, but similar studies of the copper oxide high temperature superconductors have met difficulties since positrons do not probe well the FS contribution of the Cu-O planes [5]. Another direct probe of FS is the Angular Resolved Photo-Emission Spectroscopy (ARPES) [6]. However, a concern with ARPES is that most of the information of the interacting electron liquid is based on measurements from a surface sensitive technique that can be applied only to a limited number of materials that cleave such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$. Thus, a risk is that experimental artifacts may be interpreted as fundamental physics.

At low doping, the FS signal from ARPES breaks up into Fermi arcs [7], which could be part of closed hole pockets [8, 9]. The formation of small Fermi pockets in other underdoped cuprates also emerges from quantum oscillation (QO) measurements in high magnetic fields [10–14]. These FS pieces seen by QOs could be in fact produced by FS reconstructions when some symmetry is broken [15]. According the theory by Lifshitz and Kosevich [16, 17], a period of QO is linked to an extreme cross section of the FS. Nevertheless, QOs in the layered and quasi-two-dimensional (2D) conductors may deviate from the LK theory developed for 3D conventional metals [18, 19].

Inelastic x-ray scattering [20, 21] in the deeply inelastic limit, can help to clarify the nature of the FS in copper oxide high temperature superconductors since the corresponding Compton scattering cross-section is well-known to become proportional to the ground state EMD [22]. A Compton scattering study in single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ has directly imaged in momentum space the character of holes doped into this material [23]. However, improvements in the momentum resolution are still needed to bring Compton scattering into the fold of mainstream probes for the cuprates FS. A recent Compton study of over-doped $\text{La}_{2-x}\text{Sr}_2\text{CuO}_4$ [24] shows the difficulty of extracting details of the FS with the present

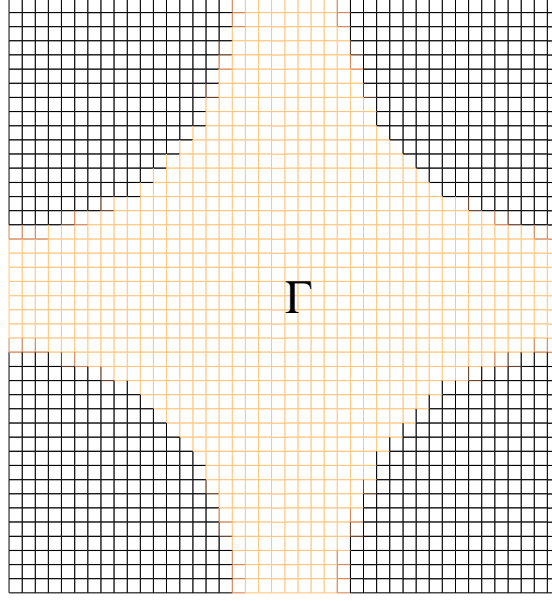


FIG. 1. The FS of $\text{HgBa}_2\text{CuO}_4$ is shown in the first Brillouin zone. It separates the occupied states (yellow grid) from the unoccupied states (black grid).

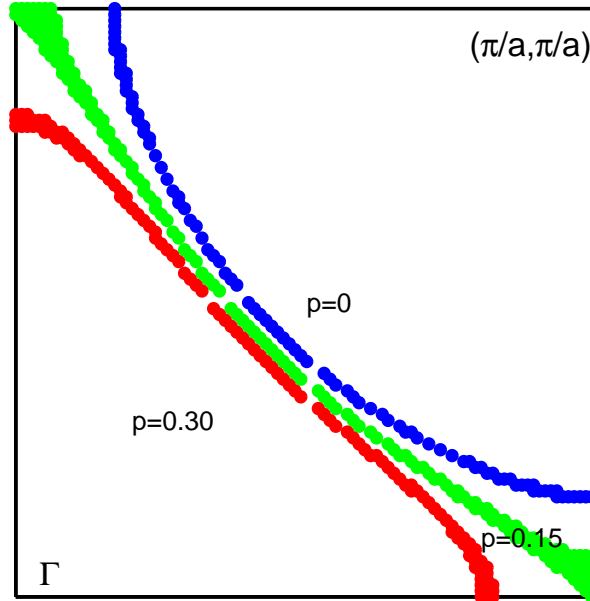


FIG. 2. Evolution of the Fermi surface in the $k_z = 0$ -plane in Ba_2CuO_3 (where one layer of apical oxygen is missing) as a function of the rigid-band doping for 0, 0.15 and 0.30 holes per unit cell. The FS evolution is almost identical in La_2CuO_4 . Only $1/4$ of the first Brillouin zone is shown. The momentum units are $1/a$, where a is the lattice constant.

momentum resolution of about 0.15 a.u. Higher momentum resolution can also allow the study of the FS smearing due to the superconducting energy gap opening [25] and to the breakdown of the Landau-Fermi liquid picture [26]. Surprisingly, Compton scattering experiments even on a simpler material such Li indicate that the EMD of the ground state is not well described by the conventional Landau-Fermi liquid framework since the size of the discontinuity Z at the FS seems to be anomalously small [27–30]. Such deviations from the standard metallic picture can be ascribed to the possible existence of significant pairing correlations in the ground state [26, 31, 32]. The notion of stabilizing the metallic state through the resonant valence bond (RVB) state dates back to the early works of Pauling, who first applied this model to the Li ground state [33]. Anderson then proposed the RVB wave function as a ground state for the high temperature superconducting materials [34], showing that this hypothesis is able of describing many aspects of the phase diagram of the cuprates [35].

This paper shows how pairing correlation effects modify the occupation of the natural orbitals [36, 37], which are used to calculate the electron momentum density [31] via a simple generalization of independent particle model (IPM). In the IPM, states are either occupied or empty [38].

The occupation numbers (corresponding to natural orbitals in Bloch states [39, 40]) are calculated through a variational scheme based on the Antisymmetrized Geminal Product (AGP) many-body wave function [26, 31, 41–46]. The AGP total energy functional is given by [31, 42, 45]

$$E_{AGP} = E_{HF} + E_{BCS} + O(1/N) , \quad (1)$$

where E_{HF} is the Hartree Fock energy functional, E_{BCS} is a BCS-type functional and N is the number of electrons in the system. Since the Coulomb interaction contained in E_{BCS} is repulsive, energy can be gained only through the exchange part E_{HF} of the Hartree-Fock functional. However, energy can also be gained through the term E_{BCS} by the introduction interactions with phonons [47]. Several authors [48–55] have considered similar functionals of natural orbitals. Nevertheless, some of these functionals violate the N -representability [31] and can become over-correlated. This problem is avoided here because the E_{AGP} is N -representable by construction.

To efficiently extract occupation numbers in a correlated electron gas, we start by approximating the natural orbitals by the Kohn-Sham orbitals [56]. For the sake of simplicity,

we suppose that the eigenvalues are described by a single energy band denoted by $\mathcal{E}_{\vec{k}}$ with μ defining the chemical potential. The result for the AGP energy functional [31] minimization gives the occupation numbers

$$n_{\vec{k}} = \frac{1}{2} \left(1 - \frac{(\mathcal{E}_{\vec{k}} - \mu)}{E_{\vec{k}}} \right), \quad (2)$$

where $E_{\vec{k}}$ is given by

$$E_{\vec{k}} = \sqrt{(\mathcal{E}_{\vec{k}} - \mu)^2 + |\Delta_{\vec{k}}|^2}. \quad (3)$$

Two self-consistent equations are also involved, one giving $\Delta_{\vec{k}}$ [57]

$$\Delta_{\vec{k}} = \frac{1}{N} \sum_{\vec{k}'} \frac{J_{\vec{k}\vec{k}'} \Delta_{\vec{k}'}}{2E_{\vec{k}}}, \quad (4)$$

and the other determining the chemical potential μ

$$N = \sum_{\vec{k}} n_{\vec{k}}. \quad (5)$$

Following Ref. [31], one can assume that $J_{\vec{k}\vec{k}'}$ is mostly given by an exchange integral. Thus, an approximation for $J_{\vec{k}\vec{k}'}$ is given by [31, 58]

$$J_{\vec{k}\vec{k}'} = \delta_{\vec{k}\vec{k}'} I_{\vec{k}}, \quad (6)$$

with

$$I_{\vec{k}} = \frac{1}{3} \int d^3\vec{r} |\psi_{\vec{k}}(\vec{r})|^4 \frac{v_x(\vec{r})}{n(\vec{r})}, \quad (7)$$

where $v_x(\vec{r}) = 2/\pi(3\pi^2 n(\vec{r})^{1/3})$ is the Kohn-Sham exchange potential [56] and $n(\vec{r})$ is the electron density. By inserting this approximation in Eq. 4, one obtains

$$\Delta_{\vec{k}}^2 = \frac{I_{\vec{k}}^2 - 4(\mathcal{E}_{\vec{k}} - \mu)^2}{4}. \quad (8)$$

Therefore $\Delta_{\vec{k}}$ is different of zero only if $I_{\vec{k}} > 2(\mathcal{E}_{\vec{k}} - \mu)$.

The calculation of the occupation numbers for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shown in Fig. 3 has been performed within an efficient linear muffin-tin orbital (LMTO) band structure method [59]. In this case, the average I is about 1.67 eV. Therefore, at the Fermi energy $\Delta \sim I/2 = 0.83$ eV. The momentum smearing produced by Δ is given by

$$\delta k = \frac{\Delta}{v_F}, \quad (9)$$

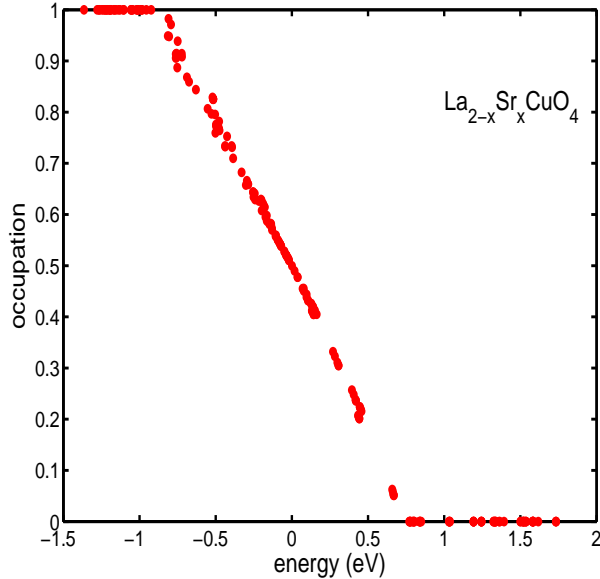


FIG. 3. Occupation number for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in the limit $x \rightarrow 0$ as a function of the Kohn-Sham eigenvalues. The Fermi level is at 0.

where v_F is the Fermi velocity. By taking $\hbar v_F \sim \pi/a$ (where $a = 7.16$ a.u. is the lattice constant) we find $\delta k \sim 0.07$ a.u. This momentum smearing is slightly below the current experimental momentum resolution of 0.15 a.u. available in Compton scattering experiments [24]. A similar δk can be produced by the antiferromagnetic order [60] when $x \rightarrow 0$, but the emergence of ferromagnetic fluctuations for $x \sim 0.25$ leads to the destruction of both RVB correlations and of the AF order in the over-doped regime [61].

In conclusion, the AGP method has been used to study the occupation numbers $n_{\vec{k}}$ of natural orbitals in Bloch states of crystals. Values of $n_{\vec{k}}$ can be extracted from EMD experiments [40] and compared to the present model. Strong modification of the occupation numbers due to pairing correlations effects are predicted for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x \rightarrow 0$ in an energy window of 0.83 eV around the Fermi energy. This effect produces a smearing of the occupation in momentum space given by $\delta k \sim 0.07$ a.u.

This work is supported by the US Department of Energy, Office of Science, Basic Energy Sciences Contract No. DE-FG02-07ER46352. It has also benefited from Northeastern University's Advanced Scientific Computation Center (ASCC), theory support at the Advanced Light Source, Berkeley, and the allocation of computer time at NERSC through Grant No. DE-AC02-05CH11231.

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